

Crossover Studies of Methyl Migration from Oxygen to Iron in the Iron–Manganese Methoxycarbyne Complex $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-COCH}_3)(\mu\text{-CO})\text{Mn}(\text{CO})\text{MeCp}$

William H. Hersh* and Raymond H. Fong†

Department of Chemistry and Biochemistry, Queens College and the Graduate Center of the City University of New York, Flushing, New York 11367-1597, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

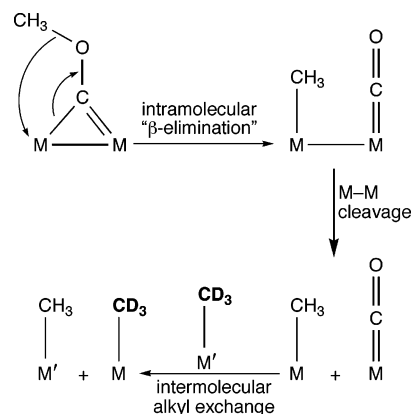
Received April 7, 2005

Thermal decomposition of the iron–manganese methoxycarbyne $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})(\mu\text{-COCH}_3)\text{Mn}(\text{CO})\text{MeCp}$ (**1a**) occurs to give $\text{MeCpMn}(\text{CO})_3$ and in low yield $\text{CpFe}(\text{CO})_2\text{CH}_3$; in the presence of PPh_3 , $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CH}_3$ (**2a**) forms in high yield. The reaction is first-order in carbyne, but a side reaction that is also first-order in phosphine occurs to give $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{Mn}(\text{CO})\text{MeCp}]^-\text{[CH}_3\text{PPh}_3]^+$ (**3a**) as a byproduct. Crossover experiments between **1a** and its bis-MeCp, CD_3 analogue **1b-d₃** result in scrambling of the methoxycarbyne methyl label between the products **2a** and the MeCp analogue **2b**. No alkyl exchange is seen in recovered starting materials in the reaction between **1a** and bis-MeCp analogue **3b** or (except after prolonged reaction) between the products **2a** and **2b-d₃**. “Control crossover” experiments between **1a** and **2b-d₃** give complete alkyl scrambling. The data prove that alkyl exchange occurs among products *after* carbyne decomposition and presumably is induced by an intermediate that is formed by carbyne decomposition. Previous results show that the 16-electron intermediate $\text{CpFe}(\text{CO})\text{CH}_3$ forms at essentially the same rate from **2a** as from **1a**, ruling it out as the exchange intermediate since **2a** and **2b-d₃** undergo only very slow exchange. A speculative proposal for the reactive intermediate is that it is the isomeric terminal methoxycarbyne $\text{CpFe}=\text{COCH}_3$, and alkyl migration from oxygen to iron occurs after cluster cleavage. A detailed kinetic scheme for alkyl scrambling is proposed and tested by computer modeling: using an iterative procedure that couples numerical integration of the proposed rate equations with a simplex minimization algorithm designed to find the best rate constants, concentration data from several runs could be quantitatively fit to the proposed mechanism.

Introduction

Many reactions in organometallic chemistry can be explained and even predicted by a relatively small set of now familiar mechanistic types, such as oxidative addition, reductive elimination, migratory insertion, and substitution.¹ Mechanistic studies of newly discovered reactions typically involve efforts to find combinations of these known basic steps that can then explain the new reaction. Because some of these elementary reaction types require that the reaction be intramolecular, a critical study is often the crossover experiment. That is, does a particular fragment remain bound to the same metal atom throughout the course of the reaction, or does it migrate to another metal atom?^{2,3} Many years ago we reported a new reaction, in which the methyl group of a bridging methoxycarbyne ligand migrated

Scheme 1. Methyl Migration in Methoxycarbyne Complexes



from oxygen to one of the metal atoms (Scheme 1),^{4,5} and since that time we have reported a few more examples of this reaction.^{6–8} In a formal sense, this

* Address correspondence to this author at Queens College. E-mail: william_hersh@qc.edu.

† Current address: Department of Chemistry, City College of San Francisco, 50 Phelan Ave., San Francisco, CA 94112.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113–120.

(3) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451–7461.

(4) Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468–1470.

(5) Fong, R. H.; Lin, C. H.; Idmoumaz, H.; Hersh, W. H. *Organometallics* **1993**, *12*, 503–516.

(6) Wang, B.; Hersh, W. H.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1319–1330.

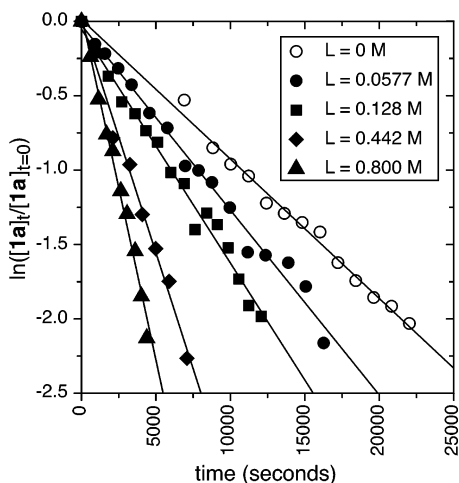


Figure 1. First-order plots of decomposition of **1a** at 75 °C as a function of PPh₃ concentration ($L = \text{PPh}_3$).

methyl migration can be thought of as a β -elimination reaction, which if literally true would require the reaction to be *intramolecular*. However, crossover experiments showed the products to be due, formally, to *intermolecular* migration. Methyl exchange was shown to be occurring *after* product formation, leaving unsettled the question of molecularity of the migration. As indicated in Scheme 1, methyl exchange presumably is mediated by a 16-electron “M-Me” fragment, which in this case might most simply be imagined to be the CpFe(CO)Me species. In this paper we describe the mechanistic experiments designed to unravel these migration processes.

Results

Kinetics of Thermal Decomposition. First-order decomposition of **1a** occurred at a convenient rate at 75 °C in C₆D₆ and was observed both in the absence and in the presence of triphenylphosphine. Under pseudo-first-order conditions (at least a 5-fold excess of PPh₃), linear plots of $\ln[\mathbf{1a}]$ vs time were obtained (Figure 1); all the reactions were monitored for three half-lives. Observed rate constants are given in Table 1 (runs 1–5). A plot of the pseudo-first-order rate constants (k_{obs}) vs [PPh₃] was linear with a nonzero intercept (Figure 2), which, within experimental error, gave the same rate constant as that measured in the absence of PPh₃ (run 1). That is, the phosphine-independent pathway has the same rate constant as that of simple thermal decomposition. The observed rate law is given in eq 1.

$$\frac{-d[\mathbf{1a}]}{dt} = (k_1 + k_2[\text{PPh}_3])[\mathbf{1a}] \quad (1)$$

$$k_1 = (9.8 \pm 0.4) \times 10^{-5} \text{ s}^{-1}, \quad k_2 = (4.64 \pm 0.09) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

The reaction products and the simplest mechanistic interpretation of the above rate data are shown in Scheme 2; characterizations of starting materials and products have been described previously.⁵ Methyl mi-

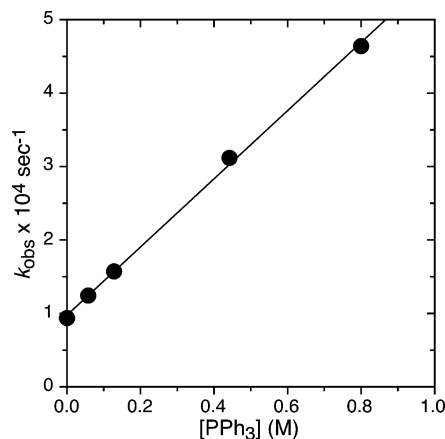


Figure 2. Plot of observed first-order rate constants (k_{obs} , 75 °C) for decomposition of **1a** vs PPh₃ concentration.

gration with concomitant metal–metal bond cleavage yields MeCpMn(CO)₃ and the 16-electron fragment CpFe(CO)CH₃. In the absence of PPh₃, decomposition of CpFe(CO)CH₃ apparently leads to loss of CO, which is then scavenged to give low yields of CpFe(CO)₂CH₃ and [CpFe(CO)₂]₂, while loss of the alkyl residue can lead to the tetrameric cluster [CpFe(CO)]₄.⁹ In the presence of PPh₃, the 16-electron species is trapped to give CpFe(CO)(PPh₃)CH₃ (**2a**). Independent synthesis of MeCpMn(CO)₂PPh₃¹⁰ showed that it did not form in these reactions of **1a**,⁵ requiring that the carbyne directly yields MeCpMn(CO)₃ and CpFe(CO)CH₃, rather than MeCpMn(CO)₂ and CpFe(CO)₂CH₃ which then exchange a CO ligand; formation of MeCpMn(CO)₂PPh₃ from MeCpMn(CO)₃ and PPh₃ occurs photochemically but not thermally (even at 140 °C).^{10–12} At high concentrations of PPh₃, dealkylation is the major reaction, giving [Cp(CO)Fe(μ -CO)₂Mn(CO)MeCp]–[CH₃PPh₃]⁺ (**3a**). On the basis of yields of MeCpMn(CO)₃ and **2a** (see Supporting Information), the reaction pathway that is zero-order in PPh₃ yields iron-alkyl **2a**, while the reaction pathway that is first-order in PPh₃ yields [Cp(CO)Fe(μ -CO)₂Mn(CO)MeCp]–[CH₃PPh₃]⁺ (**3a**). At 0.1 M PPh₃ we calculate on the basis of eq 1 that ~68% of the decomposition of **1a** occurs via the phosphine-independent pathway to give **2a**; for convenience approximately this concentration was used for all subsequent crossover reactions.

Carbyne Crossover Experiments. Crossover experiments were carried out next as shown in Scheme 3. The doubly labeled analogue **1b-d₃**, in which the Cp ligand on iron was replaced by the MeCp ligand and the methoxy CH₃ group by the CD₃ group, was allowed to decompose in the presence of **1a** and ~0.1 M PPh₃ (Table 1, run 6). After 30 min reaction at 65 °C, ~5% decomposition of the starting carbynes had taken place, and the alkyl label in the products **2a** and **2b** was found to be essentially completely scrambled between the CpFe and the MeCpFe centers, as judged by ¹H NMR examination of their methyl signals. At 200 MHz, the

(9) Landon, S. J.; Rheingold, A. L. *Inorg. Chim. Acta* **1981**, *47*, 187–189.

(10) Nyholm, R. S.; Sandhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1963**, 5916–5919.

(11) Angelici, R. J.; Loewen, W. *Inorg. Chem.* **1967**, *6*, 682–686.

(12) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61–73.

(7) Idmoumaz, H.; Lin, C. H.; Hersh, W. H. *Organometallics* **1995**, *14*, 4051–4063.

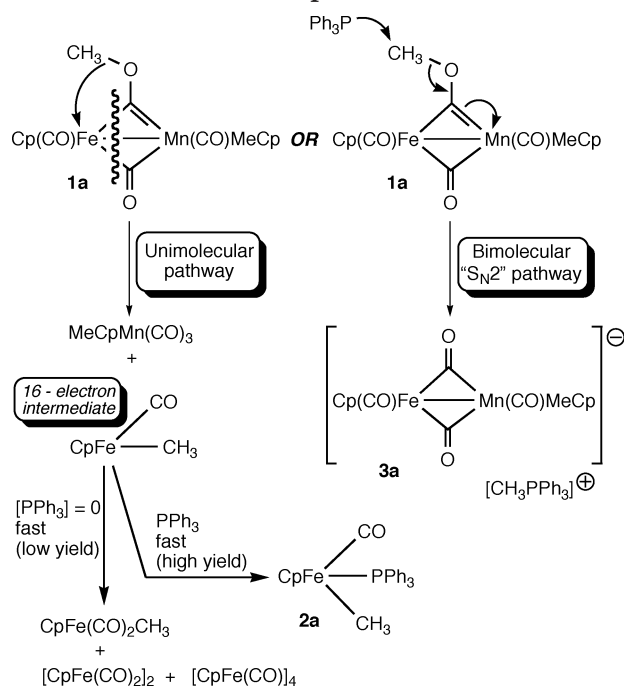
(8) Luo, W.; Fong, R. H.; Hersh, W. H. *Organometallics* **1997**, *16*, 4192–4199.

Table 1. Summary of Experimental Data: Rate Constants for Carbyne Decomposition and Carbyne and Product Crossover Results^a

run	[1a] (M)	[PPh ₃] (M)	additive (M)	10 ⁴ <i>k</i> (s ⁻¹) ^a	crossover ^b
1	0.028	0		0.937 ± 0.022	
2	0.010	0.0577		1.24 ± 0.04	
3	0.025	0.128		1.57 ± 0.05	
4	0.021	0.442		3.12 ± 0.12	
5	0.032	0.800		4.64 ± 0.16	
6	0.022	0.12	1b-d₃ (0.022)	0.48 ± 0.01	yes (~100% exchange after 0.5 h, ~5% conversion of 1a and 1b-d₃)
7	0.016	0.089	1b-d₃ (0.017)	1b-d₃ : 0.316 ± 0.007	yes (1 h 75 °C, 65% exchange after 44 ± 5% conversion of 1 ; no crossover in 1 (<2% exchange of CH ₃ and CD ₃ in recovered 1) ^c
8		0.12	2a (0.017) 2b-d₃ (0.014)		no (20 h; 51% exchange after 285 h, 80 °C)
9	0.026	0.12	2b-d₃ (0.028)	0.69 ± 0.04	yes (31% exchange after 0.5 h, 10% conversion of 1a ; ~100% exchange after 8 h, 81% conversion of 1a)
10	0.026	0.16	2b-d₃ (0.063)	0.78 ± 0.04	yes (47% exchange after 0.7 h, 23% conversion of 1a ; 64% exchange after 6 h, 85% conversion of 1a)

^a All data collected in C₆D₆, at 75 °C for runs 1–5 and run 7, and at 65 °C for the rest. Except as noted, rate constants are for decomposition of **1a**. ^b Crossover of alkyl label between **2a** and **2b**. Complete crossover is 100% exchange (see Experimental Section). ^c See Experimental Section for further details of this run.

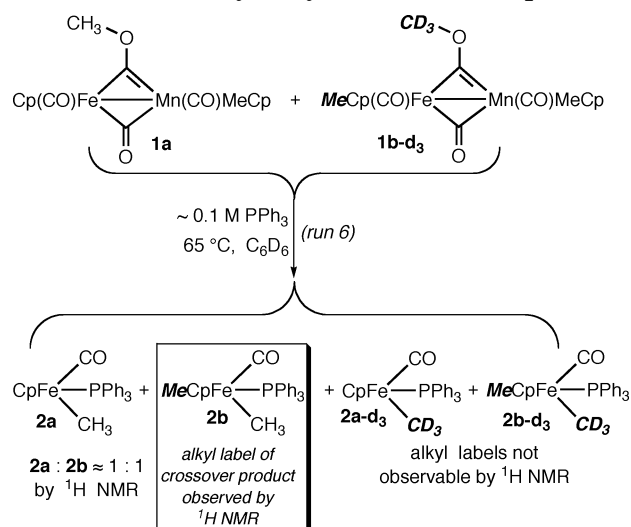
Scheme 2. Thermal Methoxycarbyne Decomposition



observed doublets (due to coupling to the PPh₃ phosphorus atoms) overlapped so that one line of each was coincident, but comparison of the peak heights or integrals of the first and third lines allowed the extent of scrambling to be determined (see Experimental Section). Monitoring of the reaction by ¹H NMR showed the two carbynes to decompose at comparable rates, and the presence of **2a-d₃** and **2b-d₃** was inferred from integration of the Cp and MeCp peaks. Simple first-order plots gave excellent linear fits and the rate constants shown in Table 1, although these values are likely to be slightly erroneous due to the fact that only a 3-fold excess of PPh₃ was used in this run. The reaction was followed to close to completion (~13 h), and complete methyl exchange occurred throughout.

While the crossover experiment between the doubly labeled carbynes shown in Scheme 3 resulted in inter-

Scheme 3. Methoxycarbyne Crossover Experiment



molecular alkyl exchange in the mononuclear products, it did not address the question of when or how the exchange occurred. A variety of control experiments were carried out to determine at what stage of the reactions the methyl exchange was occurring.

Methoxycarbyne Crossover Control Experiments. 1. Carbyne Crossover. Four control experiments were conducted to investigate methyl exchange prior to carbyne decomposition. A rational mechanism would involve a chain reaction between trace amounts of the CH₃PPh₃⁺ salts of the dinuclear anions (**3a-CH₃PPh₃⁺** and **3b-CH₃PPh₃⁺**) formed in situ and the carbynes as shown in Scheme 4. However, no crossover was observed between **1a** and **3b** or between **1b-d₃** and **3a**, and as a check, **3a** did not *inhibit* crossover in the reaction of **1a** and **1b-d₃** (see Supporting Information for details).

This anion exchange mechanism would give not only product crossover but also crossover in the starting materials. The standard control experiment, in which the crossover reaction of **1a** and **1b-d₃** was run to partial conversion and then the unreacted starting carbynes examined for alkyl exchange, was carried out (eq 2,

Scheme 4. Potential Anion-Mediated Crossover Mechanism

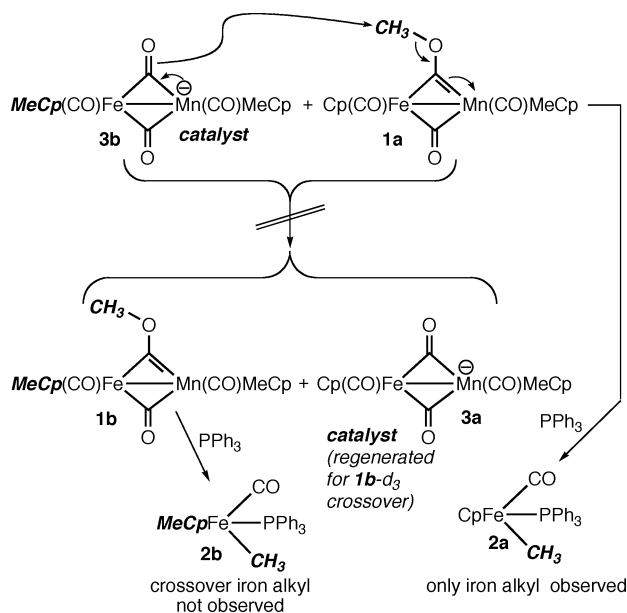
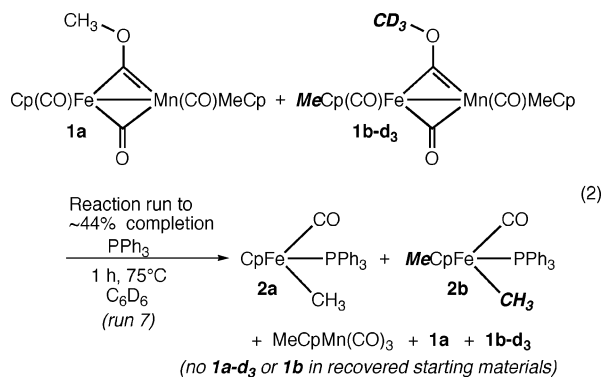


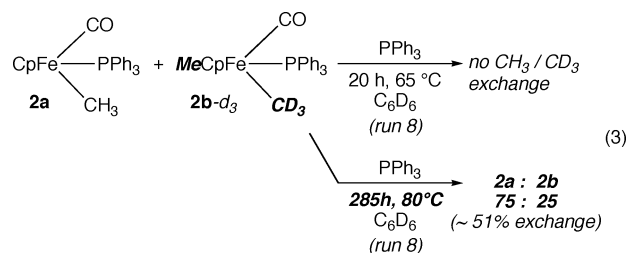
Table 1, run 7), since this would allow the detection of alkyl scrambling among starting materials regardless of the molecular details of any exchange. After 44%



consumption of the carbynes, the extent of scrambling of the methyl label in products **2a** and **2b** was 65% complete, while no exchange was detected in the recovered starting materials. The carbynes were isolated by chromatography, and the mixture was analyzed by electron ionization mass spectrometry. Large molecular ion signals were observed for **1a** ($m/e = 382$) and **1b-d₃** ($m/e = 399$), but no peaks larger than 2% of these molecular ions plus their $M + 1$ peaks were observed at 396 corresponding to **1b** or at 385 corresponding to **1a-d₃**.

A final possibility could be that alkyl exchange among the carbynes occurs concomitant with carbyne decomposition, so that the unreacted carbynes would not exhibit crossover. However, such a scheme would give bimolecular decomposition kinetics, and only unimolecular kinetics are observed. While it can be argued that NMR kinetics are not sufficiently precise to observe the curvature in a log plot that would be indicative of bimolecular kinetics, in fact similar rate constants have been observed in some runs where fairly different starting concentrations of the carbynes were used; for instance in run 1 [**1a**] was 2.8 times [**1a**] in run 2.

2. Product Crossover. Alkyl exchange also can in principle occur after carbyne decomposition occurs, among the mononuclear products. The required control experiment involves checking for crossover in the products **2a** and **2b-d₃**. Under the same reaction conditions used for the crossover reaction between **1a** and **1b-d₃**, that is, after 3 h at 65 °C in the presence of ~0.1 M PPh₃, no signal due to the FeCH₃ hydrogens of **2b** was visible (run 8, eq 3), and hence crossover is not due to simple methyl exchange among the reaction products. Even after 20 h at 65 °C no **2b** was observed, but

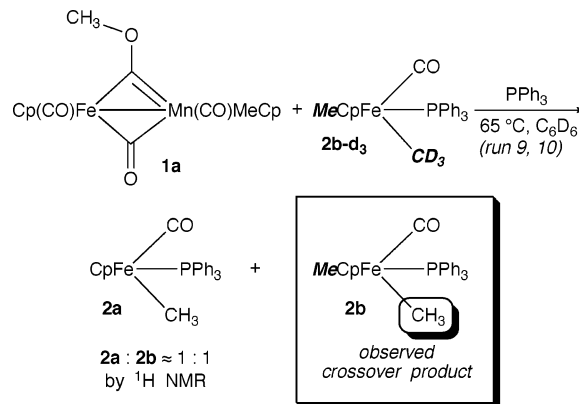


prolonged reaction at 80 °C did lead to slow exchange (run 8, eq 3), suggesting that **2a** and **2b** slowly yield an intermediate that could lead to methyl crossover. However, no exchange could be induced by **3a** or MeCpMn(CO)₃, and in one run where **3a** was introduced, CpFe(CO)(PPh₃)H was detected but still no exchange occurred (see Supporting Information for details). In conclusion, methyl exchange could not be induced to occur in the absence of carbyne except after prolonged heating. Examination of the mechanism of this exchange awaits further study, but it cannot be assumed to be the same as that observed in the presence of the carbynes.

3. Carbyne/Product Crossover. The key crossover experiment, dubbed the “control crossover”, was designed to check the role of the *carbyne* rather than any of the decomposition products in crossover. Here carbyne **1a** was mixed with “product” **2b-d₃** (Scheme 5), and in sharp contrast to the absence of reaction between products **2a** and **2b** in eq 3, *complete scrambling was observed at 65 °C within 8 h* (run 9). Since no **1b** was present, the crossover product **2b-h₃** formed could not arise due to intermolecular methyl migration from the methoxycarbynes.

Monitoring this reaction by ¹H NMR showed that while apparent equilibration of **2a** and **2b** occurred, there appeared to be an induction period. That is, at 30

Scheme 5. Control Crossover Experiment



min the extent of exchange was 30% that expected at equilibrium, and this gradually rose to about 90% after 3 h reaction, when half of the carbyne had been consumed. In this experiment, as in virtually all of the others, approximately equal amounts of the CH₃ and CD₃ components were used, so at equilibrium, if in fact an equilibration was involved, similar amounts of **2a** and **2b** would be expected. If there is an equilibration step, use of excess **2b-d₃** might initially yield more **2b** than **2a**. A control crossover experiment was therefore run in which the initial ratio **2b-d₃**:**1a** was 2.5:1 rather than 1:1 (run 10). The observed result was little changed (Scheme 5): initially more **2a** than **2b** formed, and as the reaction progressed, the amount of **2b** formed approached that of **2a**, although in this run the final extent of "equilibration" was less than 70%. The major difference between runs 9 and 10 was found in the relative amounts of **2a** and **2a-d₃**: in the 1:1 **2b-d₃**:**1a** experiment (run 9), equal amounts of **2a** and **2a-d₃** formed, while in the 2.5:1 experiment (run 10), the ratio of **2a-d₃**:**2a** was about 2:1. That is, the distribution of methyl label in **2a** did behave as though it was due to equilibration, but the distribution of label in **2a** and **2b** did not.

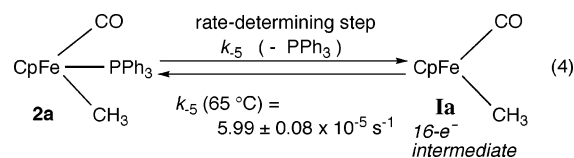
Discussion

1. Constraints. The results described above are complex and severely restrict the available mechanisms. Facts that have been established are (1) methyl exchange occurs between carbynes only upon carbyne decomposition—no exchange is detected in unreacted carbynes, (2) methyl exchange is essentially complete at early reaction time for the carbyne crossover, (3) methyl exchange among the mononuclear products in the first few hours of reaction occurs only in the presence of carbynes, and (4) under all conditions, roughly equivalent amounts of the CH₃ methyl exchange products form, even when the initial amounts of CH₃ and CD₃ starting materials differ substantially.

The most straightforward conclusion that follows from the above facts is that a carbyne decomposition product is involved in the methyl exchange reaction. We have established that MeCpMn(CO)₃ is extruded from the carbyne without formation of any MeCpMn(CO)₂PPh₃ that would arise from MeCpMn(CO)₂ (Scheme 2), leaving behind the elements of CpFe(CO)CH₃—either in this form or some other—that must also be extruded from the carbyne. Since **2a** can form by trapping of CpFe(CO)CH₃ by PPh₃, this specific intermediate is an obvious candidate for involvement in the exchange reaction, and one can readily imagine how this might form by methyl migration from oxygen to iron.⁷

2. The CpFe(CO)Me Mechanism. The products **2a** and **2b-d₃** do not exchange in the absence of **1a** except after prolonged reaction. Therefore, if CpFe(CO)Me and MeCpFe(CO)Me are responsible for methyl exchange, then loss of phosphine from **2a** (and of course any of the products **2b**, **2a-d₃**, **2b-d₃**) to give these intermediates must be much slower than their formation from carbyne decomposition. While this assumption in fact seems reasonable, it was tested by directly examining the kinetics of phosphine substitution in **2a** and was found to be wrong.¹³ As shown in eq 4, rather than being slower than carbyne decomposition, the rate at 65 °C

for dissociation of PPh₃ from **2a** to give 16-electron intermediate **1a** is slightly faster than carbyne decomposition to give **2a**. The rates for decomposition of **1a**



(i.e., run 6 at 65 °C) in Table 1 include the bimolecular pathway leading to anion **3a**, while the path leading to **2a** is less than $\sim 5 \times 10^{-5} \text{ s}^{-1}$ (vide infra). The key point is that since no methyl exchange occurs between **2a** and **2b-d₃** in the absence of carbyne **1** under these conditions, CpFe(CO)CH₃ cannot be the intermediate formed from **1a** that induces methyl exchange.

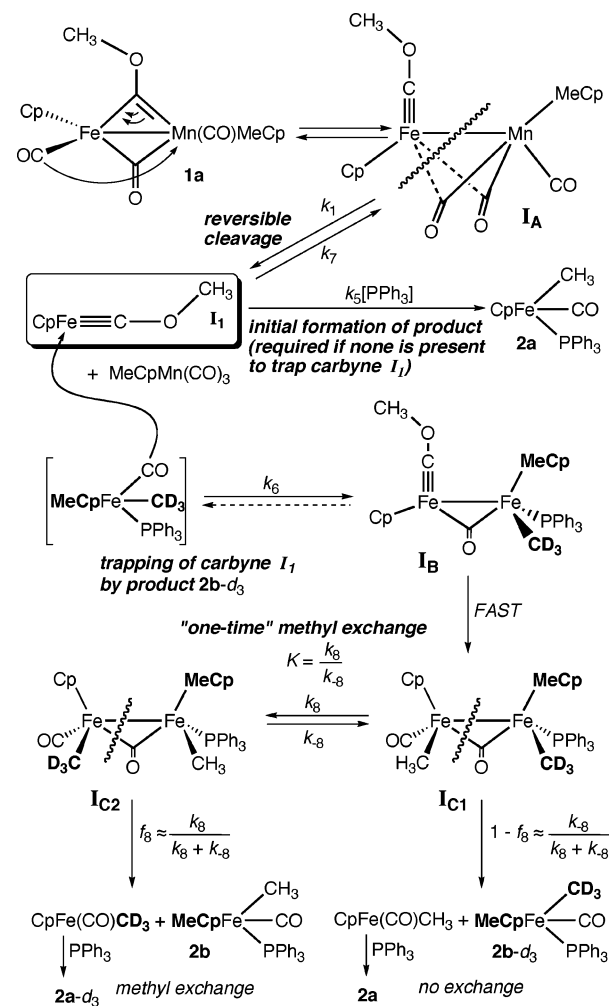
There is an additional, albeit more subtle, kinetic problem with any CpFe(CO)Me mechanism that allows it to be rejected, along with any other kinetically related mechanism in which a common intermediate leads to both product formation and methyl exchange. The degree of methyl exchange will depend on the relative rates of trapping of intermediate CpFe(CO)CH₃ by PPh₃ to give product **2a** and by **2b-d₃** which regardless of the details would be required for methyl exchange. If trapping by PPh₃ is faster, the result would be slower formation of **2b** than **2a** throughout the reaction, without attainment of equilibrium of the two products. On the other hand, if trapping of CpFe(CO)CH₃ by **2b-d₃** is faster, then the initially formed mononuclear alkyl product from **1a** would be the crossover product **2b**, not **2a**! The fact that three experiments—one starting with equal amounts of **1a** and **1b-d₃**, one with equal amounts of **1a** and **2b-d₃**, and one with **1a** and 2.5 equiv of **2b-d₃**—give essentially 1:1 ratios of **2a** and **2b** makes it unlikely that this result is due to some serendipitous set of rate constants. The conflicting requirements of product formation and equilibration require that a common intermediate cannot lead to both pathways. Further quantitative kinetic details may be found in the Supporting Information.

3. The Reversible Cleavage Mechanism. A further constraint on the mechanism was uncovered during attempts to quantitatively model the CpFe(CO)Me mechanism. Both the rate of carbyne decomposition and yields of product were reproducibly correlated with the amount of "product" initially present in solution. That is, the two-carbyne experiments always gave relatively lower rates and yields than the control crossover reactions, and the 2.5:1 **2b-d₃**:**1a** experiment gave the highest rate and yield. For instance, derived values for the first-order rates of decomposition of **1a** when each run was considered separately (see Supporting Information for details) gave the methyl migration rates after deducting the PPh₃-induced bimolecular decomposition, and these rates rose from $2.1 \times 10^{-5} \text{ s}^{-1}$ for the two-carbyne experiment (run 6) to $5.0 \times 10^{-5} \text{ s}^{-1}$ for the high-concentration control crossover (run 10). Alternatively, examination of the raw data—that is, first-order carbyne decomposition rates that include the PPh₃-induced decomposition—showed the same trend, presumably because [PPh₃] differs little from run to run: the rates rose from $4.8 \times 10^{-5} \text{ s}^{-1}$ for the two-carbyne experiment (run 6) to $7.8 \times 10^{-5} \text{ s}^{-1}$ for the high-

concentration control crossover (run 10). The final yield of **2a** and **2a-d₃** rose from 39% in the two-carbyne experiment to 61% in the 0.028 M **2b-d₃** control crossover to 75% in the 0.063 M **2b-d₃** control crossover experiment. In all three cases, the rates and yields appear to be correlated only with **[2b-d₃]**; as this concentration rises, more of the reaction is siphoned off toward the reaction of interest and less to the PPh₃ S_N2 reaction. A plot of the rates of first-order decomposition of **1a** (k_1 from Table S-4 for the individual runs in the Supporting Information or the raw rate from Table 1) vs **[2b-d₃]_{t=0}** gave parallel straight lines (slope = $(4.5 \pm 0.5) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $(4.7 \pm 1.3) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, respectively, for runs 6, 9, 10), suggesting a bimolecular component to the reaction. Since decomposition of the carbynes is first-order, this result can only occur if the carbyne is in reversible equilibrium with some intermediate that is trapped by **2b-d₃**, and this trapping is relatively slow compared to reversal back to starting material. Nonetheless, this trapping will be faster at higher initial concentrations of **2b-d₃**, and as more of the reaction is diverted to this pathway, not only will higher rates of reaction be observed, but the amount of decomposition of the carbyne to the byproduct PPh₃Me⁺ salt **3** (Scheme 2) will decrease, thereby leading to the higher observed yields since less starting material will be diverted by PPh₃.

A mechanism based on reversible carbyne cleavage is shown in Scheme 6. The initial step, production of intermediate **I_A**, is not kinetically distinguishable, but is reasonable based on prior work in which rapid cis/trans isomerization was observed; that is, following carbyne unbridging (and carbonyl unbridging, which is not shown here), rotation about the Fe–Mn bond can occur. We have previously invoked this step for other carbyne reactions in which cis/trans isomerization and phosphine attack on reversibly formed dinuclear intermediates occurs.^{6,8,14} Intermediate **I_A** consists of MeCp–Mn(CO)₃ side-bound to the iron, and it is reasonable to suggest that this species will rapidly decompose via cleavage of the $\mu\text{-CO}$ –iron bonds to give the 16-electron intermediate CpFeC≡OCH₃ (**I₁**). Precedent for expulsion of MeCpMn(CO)₃ comes from the cleavage of isoelectronic heterodinuclear compounds,^{15–18} which we have previously compared to reactions of related heterodinuclear carbyne complexes.^{6–8} Here, however, we propose that the reaction is reversible; the subsequent trapping by **2b-d₃** is similar to trapping by MeCpMn(CO)₃, and the fact that the best-fit rates for these trapping steps, k_6 and k_7 , will turn out to be quite similar (see below) lends further support for this mechanism. It is reasonable to suppose that the trapping by **2b-d₃** is similarly reversible, as shown by the dashed arrow, although it is kinetically indistinguishable from

Scheme 6. Mechanism of Carbyne Cleavage and Methyl Exchange



the irreversible trapping, and this step was not given any further consideration. While many parts of this mechanism are highly speculative, it is this portion of the proposal alone that allows the decomposition rates and the product yields to be fit reasonably well; all variants on this mechanism that do not include this reversible carbyne cleavage followed by competitive trapping do not give reasonable fits. Following trapping of **I₁** by the iron alkyls, as illustrated in Scheme 6 for **2b-d₃** to give **I_B**, we propose fast methyl migration from oxygen to iron to give a diiron dimethyl species, **I_{C1}**, which is in rapid equilibrium with **I_{C2}**; rapid cleavage to product and CpFe(CO)Me followed by trapping by PPh₃ then gives the final products. Methyl exchange in this scheme does not involve equilibration of the methyl groups among all the iron alkyl species in solution, but rather only during the trapping step in a so-called “one-time” methyl exchange.

In the absence of **2b-d₃** initially, a route to some iron alkyl must exist, since otherwise **I₁** could only revert back to **I_A** according to the mechanism thus far. A step involving isomerization of carbyne **I₁** to CpFe(CO)CH₃, followed by trapping to give **2a**, is reasonable, but there is no obvious intuitive answer to whether this will be a pathway that is competitive with the trapping pathway. That is, significant production of **2a** might come from this isomerization pathway if k_5 were large relative to k_6 . Alternatively, slow formation of **2a** along the k_5

(13) Hersh, W. H.; Hunte, F.; Siegel, S. *Inorg. Chem.* **1993**, *32*, 2968–2971.

(14) Hersh, W. H. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; Nato ASI Series C: Mathematical and Physical Sciences, Vol. 392; Kluwer Academic Publishers: Dordrecht, 1993; pp 149–150.

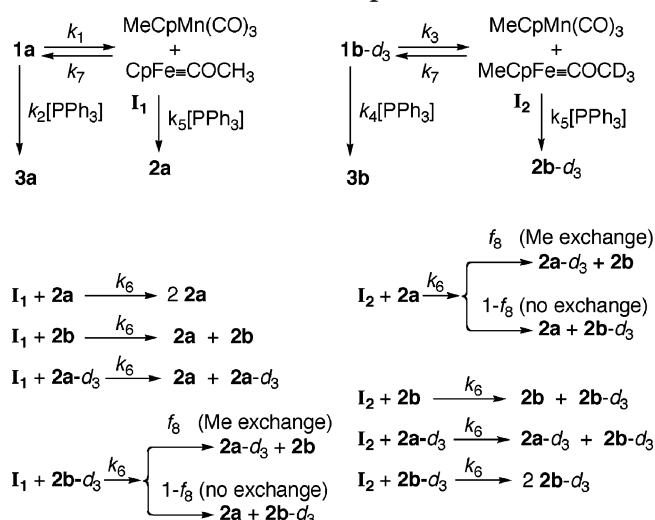
(15) Leonhard, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 649–650.

(16) Werner, H.; Juthani, B. J. *Organomet. Chem.* **1981**, *209*, 211–218.

(17) Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177–188.

(18) Aldridge, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. J. *Chem. Soc., Dalton Trans.* **1982**, 1333–1340.

Chart 1. Reaction Steps for Scheme 6



pathway would essentially give **2a** as a *catalyst* for reaction of **I₁**. That is, as soon as any **2a** forms, it would catalyze the decomposition of **I₁** by trapping to give **I_B**, which then would yield more **2a**. In the same way, **1b-d₃** will yield **2b-d₃** and methyl exchange can then proceed. Since this is an autocatalytic process, slow isomerization of **I₁** to **2a** will not be a bottleneck for decomposition of **1a**. In fact, as will be seen below, the kinetic modeling clearly favors this autocatalytic pathway, since rapid formation of **2a** from **I₁** would give far more **2a** relative to **2b** in the control crossover reactions.

The complexity of this system requires numerical modeling. The reaction steps and rate constants needed to model the mechanism in Scheme 6 are shown in Chart 1. The kinetically distinguishable steps are (1) reversible cleavage of the dinuclear carbynes to give MeCpMn(CO)₃ and the mononuclear 16-electron carbynes CpFe≡COCH₃ (**I₁**) and MeCpFe≡COCD₃ (**I₂**) by k_1 or k_3 and k_7 , (2) trapping of the intermediate mononuclear carbynes **I₁** and **I₂** by PPh₃ to give products **2a** and **2b-d₃** by k_5 , and (3) trapping of the intermediate mononuclear carbynes **I₁** and **I₂** by each of the iron alkyl products in a one-time exchange event as an alternative route to each of **2a**, **2a-d₃**, **2b**, and **2b-d₃** by k_6 . Methyl exchange occurs *only* following trapping of **I₁** by **2b-d₃** (shown in Scheme 6) and of **I₂** by **2a** (not shown in Scheme 6) to give intermediate **I_B** in the kinetically significant k_6 step, followed by several fast steps. Rather than specify each of these fast steps, the mechanism was modeled by substituting the fraction of exchange (f_8) as shown in Scheme 6 and Chart 1. That is, for instance, in terms of the microscopic fast rate constants (see Scheme 6 for k_8 and k_{-8}), if the rates of cleavage of **I_{C1}** and **I_{C2}** were equal, then the fraction of exchange would be given exactly by $f_8 = k_8/(k_8 + k_{-8})$, and the fraction that does not give exchange by $k_{-8}/(k_8 + k_{-8}) = 1 - f_8$. If methyl exchange between **I_{C1}** and **I_{C2}** is rapid and there is no thermodynamic preference for either intermediate (i.e., $K = k_8/k_{-8} \approx 1$) and if their rates of cleavage are similar, then the fraction f_8 should be close to 0.5. In addition, use of this fraction emphasizes the fact that there is only one independent variable for this step. To minimize the number of different rate constants, the same rate constants for each of the different types of trapping steps were used even though (for

instance) MeCpMn(CO)₃ would be expected to react with **I₁** and **I₂** at slightly different rates, k_7 and k_7' ; the additional rate constants were found to be unnecessary.

A computer program was written to quantitatively model the system, using known numerical routines to (1) numerically integrate the coupled set of differential equations for the reactions in Chart 1, using a fourth-order Runge–Kutta method with adaptive step-size control, (2) calculate the deviation of the values of the calculated time points from the observed (see Experimental Section for details of the error function χ_v^2), and (3) iteratively adjust the rate constants using a simplex minimization algorithm to give the best-fit set of rate constants simultaneously for all the runs.¹⁹ The program, dubbed CRK2005 (“Complex Reaction Kinetics”, updated from previous versions^{20,21}), requires input of the differential equations, the initial concentrations of all species, and guesses for each rate constant. In addition, since all the calculated concentrations depend on the initial values input at zero time, CRK2005 allows initial concentrations to be adjusted to give the best fit; in practice, only the initial concentration of **1a** was varied (by up to ~5%). Since this is a steady-state system, only the ratio of the “fast” rate constants k_5/k_6 and k_7/k_6 can be determined, although in practice due to the complexity of the equations, the steady-state approximation was not used. Instead, rate equations for each reaction species were used rather than algebraically eliminating the intermediates, the concentrations of which were constrained to be less than 0.01% of the highest concentration in a kinetic run. While there is no obvious precedent for a guess at the value of k_6 , it is reasonably lower than that for the reaction of CpFe(CO)Me and PPh₃. Use of Wrighton’s²² lower limit of $3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ required unreasonable amounts of computer time in order to successfully integrate equations with rate constants that differed by ~8 orders of magnitude, and the rate could be higher, given Ford’s²³ value of $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for trapping by CO. Nevertheless, values of k_6 below even $1 \text{ M}^{-1} \text{ s}^{-1}$ gave identical results with far less computer time, apart from the concentrations of the intermediates, although in order to keep these concentrations below the 0.01% level, typical values of k_6 were greater than $100 \text{ M}^{-1} \text{ s}^{-1}$.

Use of the equations from Scheme 6/Chart 1 in CRK2005 gave an excellent fit to the observed data for runs 6, 9, and 10. The observed data and calculated lines using rate constants k_1 – k_7 and f_8 are shown in Figure 3a–c, giving an overall deviation $\chi_v^2 = 0.952$ for 191 nonzero data points (and an average error of 9.17%; see Experimental Section for an explanation of these error functions). A mechanism based on CpFe(CO)Me intermediates, previously discarded as described above, could also be numerically modeled and not surprisingly gave much higher errors of $\chi_v^2 = 3.12$ and an average error of 16.7% (see Supporting Information for details). Of

(19) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes: The Art of Scientific Computing*; Cambridge University Press: Cambridge, 1986.

(20) Bonnesen, P. V.; Baker, A. T.; Hersh, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 8304–8305.

(21) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070–6081.

(22) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602–611.

(23) McFarlane, K. L.; Ford, P. C. *Organometallics* **1998**, *17*, 1166–1168.

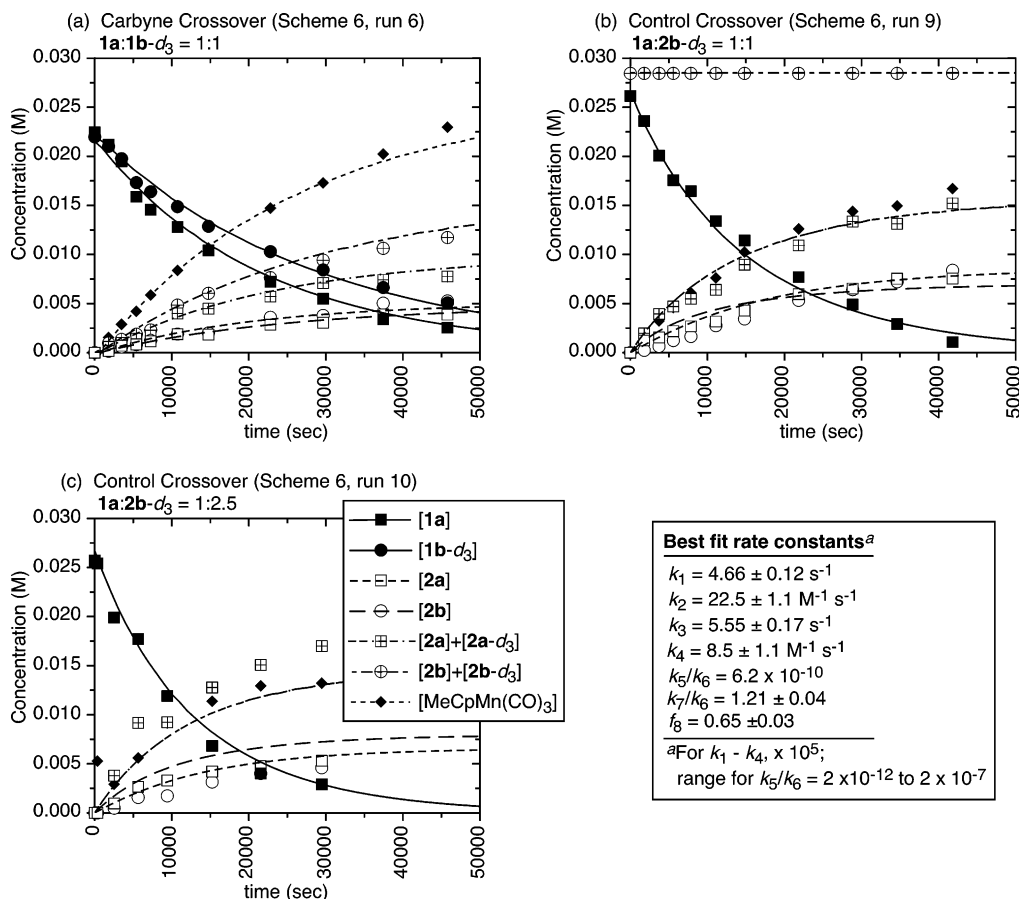


Figure 3. Best fit of mechanism in Scheme 6, using the equations from Chart 1, to observed concentration data for runs 6, 9, and 10. The calculated lines for **[2a]** + **[2a-d₃]** and MeCpMn(CO)₃ are coincident for runs 9 and 10, and the line for **[2b]** + **[2b-d₃]** at 0.063 M is not shown in run 10; it is an exact fit just as seen for the 0.028 M line for **[2b]** + **[2b-d₃]** in run 9.

interest is (1) the value of k_1 is $4.66 \pm 0.12 \text{ s}^{-1}$, which allows each of the three runs to fit the rate of decomposition of PPh₃ from **2a** (eq 3), (2) the data may be fit with a wide range of values of k_5/k_6 with values of k_5 that are many orders of magnitude less than k_6 , so as described above the k_5 step is clearly indicative of an autocatalytic reaction, (3) k_6 and k_7 are comparable in value, consistent with trapping of reactive carbyne **I**₁ with either **2a**, **2b**, or MeCpMn(CO)₃, (4) the best fit gives $f_3 = 0.65 \pm 0.03$, not far from the expected value of ~ 0.5 , and (5) allowing different rate constants to be used for the different trapping steps (i.e., k_7 for **I**₁ and MeCpMn(CO)₃ and k_7' for **I**₂ and MeCpMn(CO)₃, or variations in k_6 for the different trapping combinations of **I**₁ and **I**₂ with **2a** and **2b**, for instance) did not improve the fit, thereby keeping the overall number of parameters required to a respectably small value.

4. Kinetics Leftovers. While the overall fit of the data to the proposed mechanism is good, it is not perfect, and so the question arises: is the mechanism still incomplete or imperfect, or are the data imperfect? For instance, the mechanism does not reproduce the observed induction period in which more **2a** forms than **2b** at the outset of the reaction in the control crossover reactions. Indeed, for the high-concentration **2b-d₃** run, the best fit leaves the concentration of **2b** higher than **2a** throughout the run, the opposite of what was observed. Also as previously noted for run 10 (Scheme

5), the calculated ratio of **2a-d₃**:**2a** was lower than that observed, for instance, as seen in Figure 3c, where the calculated line for **2a-d₃** + **2a** is lower than the observed data. Up to this point in the mechanism, there are no "extra" steps or rate constants. That is, while common wisdom is that *any* reaction can be fit given sufficient number of mechanistic steps and rate constants, no extraneous steps have been described thus far. Indeed, we have attempted to minimize the proliferation of rate constants, for instance as noted above by setting the trapping rates for CpFe and MeCp analogues equivalent to each other (i.e., k_6 and k_7). In this case, it is probably best to conclude that while the data are sufficiently consistent to point toward some mechanistic detail that is yet uncovered, the data are also sufficiently imperfect to not warrant further incorporation of additional mechanistic steps.

5. Terminal Methoxycarbynes, Related μ -Carbynes, and Alkyl Migration. A brief review of related carbynes, both terminal (observed and proposed) and bridging, as well as their observed and proposed migration chemistry, is in order. We are aware of only one report of a terminal methoxycarbyne, that is, a stable 18-electron analogue of CpFe≡COCH₃ (**I**₁) and MeCpFe≡COCD₃ (**I**₂), namely, Tp'(CO)₂W≡COCH₃ reported by Templeton.²⁴ A number of sulfur analogues, that is,

(24) Stone, K. C.; White, P. S.; Templeton, J. L. *J. Organomet. Chem.* **2003**, *684*, 13–19.

terminal methylthiocarbonyls, were described years ago by Angelici,^{25,26} and terminal siloxycarbonyls have been described by Lippard.^{27,28} Templeton's carbonyl acts as an electrophilic methylating agent, eliminating the relatively stable anion $\text{Tp}'(\text{CO})_3\text{W}^-$; such a pathway could provide a mechanism for oxygen to methyl migration by intermolecular methyl transfer, but is unlikely for the putative 16-electron iron carbonyls, which would have to eliminate the 16-electron anion $\text{CpFe}\equiv\text{CO}^-$ or perhaps $\text{CpFe}(\text{PPh}_3)\text{CO}^-$, neither of which would be reasonable and for good measure would be even less likely in our case due to the use of benzene as the solvent.

We are not aware of any other reports of methyl migration from oxygen to metal in μ -methoxycarbonyls other than those that we have described.^{6–8} Ford²⁹ and Seyferth³⁰ have described examples of alkyl migration in μ -alkoxycarbonyls from oxygen to the neighboring carbon to give μ -acyl compounds. Such an unconventional 1,2-shift could serve as an alternative route to methyl migration to the metal since subsequent "normal" carbonyl deinsertion could then occur via alkyl migration from the acyl to the metal, or the "1,2-shift" could be a product of our equally unconventional initial alkyl migration from the carbonyl oxygen directly to the metal followed by "normal" carbonyl insertion via alkyl migration back to the carbonyl. While we have considered acyl intermediates in our mechanistic schemes, we see no advantage or necessity for such intermediates, and there is no evidence for the formation of $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{FeC}(\text{O})\text{CH}_3$ ³¹ in any of our reactions.

A potential example of methyl migration might reasonably be sought from the variety of A-frame dimetal compounds that have been reported with μ -methoxycarbonyl, hydroxycarbonyl, and methylene ligands, σ -alkyl ligands, hydrides, and acyl ligands.^{32–40} In none of these cases have interconversions of carbonyl and alkyl ligands been observed. Gladfelter reported the first set of strictly isomeric μ -methoxycarbonyl and σ -Me compounds, and these diruthenium compounds did not exhibit any

interconversion by ¹H NMR spectroscopy.³² No reactions of the carbonyl were described, while the methyl complex could be carbonylated to give an acyl complex. While not A-frame compounds, Ruiz has reported the second pair of isomeric μ -methoxycarbonyl and in this case μ -Me compounds, but no reactions of these dimolybdenum PCy_2 -bridged compounds were reported.⁴¹ Cowie has reported an extensive series of A-frame compounds, some of which are cited above; perhaps the closest analogues involve a diiridium system in which σ -methyl and σ -methoxymethyl complexes were synthesized, and in the latter case double C–H insertion gave an unreactive μ -methoxycarbonyl dihydride.³⁷ In addition, Cowie has reported heterodinuclear compounds that undergo methyl migration from one metal to the other,^{35,39,40} so at least that step in our mechanism has precedent.

In addition to the 1,2-oxygen to carbon alkyl migration reactions described above, a few related migration examples have been described or proposed. One involves reaction of metal anions with Fischer-type methoxycarbonyl carbenes to give intermolecular methyl transfer and an anionic acyl complex⁴² in a reaction that is comparable to demethylation of Templeton's methoxycarbonyl with expulsion of $\text{Tp}'(\text{CO})_3\text{W}^-$; as noted above this pathway seems unlikely for our carbonyls and was shown *not* to occur between the dinuclear anions **3** and the dinuclear carbonyls **1**. Several examples have been proposed in which a silicon group migrates from iron to an acyl oxygen to give a carbene,^{43,44} while in two catalytic CO reductions by hydrosilanes, a step was proposed that is the reverse of our methyl migration, in which a silyl moiety migrates from metal to the oxygen of a bound carbonyl to give a terminal siloxycarbonyl.^{45,46} Decomposition of some silyl-substituted Fischer-type carbenes has been proposed to proceed by migration first of the silicon to the metal to give a terminal alkoxycarbonyl, followed by migration of the alkyl group to the metal.^{47,48}

One conclusion from the above is that dinuclear systems with sufficient stability to exist both as the isomeric carbonyl and methyl carbonyl compounds^{32,41} may not exhibit interconversion of these species. However, the bridging acyls may be on the same reaction pathway, although like our system, there is no detail on the mechanism of the actual migration reaction itself.^{29,30} The proposal of the intermediacy of a terminal methoxycarbonyl now has precedent with the observation of the first isolable example,²⁴ and the intramolecular migration of the methyl from oxygen to iron is supported by a small number of examples in both the

(25) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397–2402.

(26) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983–2988.

(27) Vrtis, R. N.; Liu, S.; Rao, C. P.; Bott, S. G.; Lippard, S. J. *Organometallics* **1991**, *10*, 275–285.

(28) Vrtis, R. N.; Bott, S. G.; Lippard, S. J. *Organometallics* **1992**, *11*, 270–277.

(29) Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 551–558.

(30) Seyferth, D.; Ruschke, D. P.; Davis, W. M. *Organometallics* **1994**, *13*, 4695–4703.

(31) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258–264.

(32) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1990**, *9*, 2101–2105.

(33) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550–2559.

(34) Sterenberg, B. T.; Hiltz, R. W.; Moro, G.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **1995**, *117*, 245–258.

(35) Antwi-Nsiah, F. H.; Oke, O.; Cowie, M. *Organometallics* **1996**, *15*, 1042–1054.

(36) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1999**, *18*, 634–641.

(37) Torkelson, J. R.; Oke, O.; Muritu, J.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 854–864.

(38) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Robert, F. *Organometallics* **2002**, *21*, 1177–1183.

(39) Trepanier, S. J.; McDonald, R.; Cowie, M. *Organometallics* **2003**, *22*, 2638–2651.

(40) Rowsell, B. D.; McDonald, R.; Cowie, M. *Organometallics* **2004**, *23*, 3873–3883.

(41) García, M. E.; Melón, S.; Ramos, A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983–1985.

(42) Toomey, L. M.; Atwood, J. D. *Organometallics* **1997**, *16*, 490–493.

(43) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325–1332.

(44) Knorr, M.; Braunstein, P.; Decian, A.; Fischer, J. *Organometallics* **1995**, *14*, 1302–1309.

(45) Chatani, N.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **1993**, *115*, 11614–11615.

(46) Chatani, N.; Shinohara, M.; Ikeda, S.; Murai, S. *J. Am. Chem. Soc.* **1997**, *119*, 4303–4304.

(47) Schubert, U.; Hörnig, H. *J. Organomet. Chem.* **1987**, *336*, 307–315.

(48) Schubert, U. *J. Organomet. Chem.* **1988**, *358*, 215–228.

forward and reverse direction, for both silyl^{45,46} and alkyl^{47,48} migration.

Conclusion

We have discovered a series of heterodinuclear alkoxy-carbyne complexes that undergo a novel migration reaction in which the alkyl group migrates from oxygen to iron.^{4–8,14} In the study reported here, we have carried out our most extensive series of control experiments to uncover the mechanism of this migration and the concomitant methyl scrambling that occurs and coupled that with the first detailed kinetic analysis of the results. The computer methods used are applicable to a broad range of organometallic mechanisms, and in this case are necessary since the systems are too complex to quantitatively determine if a given mechanism really “fits”. In fact, the common wisdom that *any* mechanism can be fit, given sufficient numbers of steps and rate constants, seems to meet its match in this carbyne decomposition, where the most surprising conclusion is that no simple “natural” mechanism can yield equal amounts of the methyl-scrambled products. The proposal that a reactive 16-electron isomer of the venerable CpFe(CO)CH₃ intermediate forms, namely, the terminal methoxycarbyne CpFe≡COCH₃, warrants scrutiny, although it is not clear if it can be trapped in any way that preserves the terminal methoxycarbyne moiety. Finally, the question that we started with, namely, the intra- or intermolecular nature of the methyl migration from oxygen to iron, remains unanswered. We have shown that the decomposing carbyne mediates methyl exchange with the final reaction products, but we cannot tell if the initial migration is to the iron of the terminal methoxycarbyne or to another iron atom. However, since we have also shown that the 16-electron intermediate CpFe(CO)CH₃ alone does *not* mediate methyl scrambling, isomerization of CpFe≡COCH₃ to CpFe(CO)CH₃ can occur only *after* methyl scrambling has occurred, and so the proposed terminal methoxycarbyne apparently plays a key role in the methyl exchange reaction.

Experimental Section

General Procedures. Experimental methods were the same as those described in detail previously.⁵ Compounds **1a**, **1b-d₃**, **3a-Na⁺**, **3a-CH₃PPh₃⁺·CH₂Cl₂**, and **3b-CH₃PPh₃⁺·CH₂Cl₂** were prepared as we have previously described,⁵ and methods and data for **2a**, **2b**, and **2b-d₃** have been reported previously.^{5,6} Triphenylphosphine was recrystallized from ethanol, Ph₃CH was recrystallized from hexane, and CH₃-PPh₃⁺Br⁻ (Aldrich) and MeCpMn(CO)₃ (Aldrich) were used as received.

¹H NMR Reactions. General. In the glovebox, reactants were loaded into an NMR tube that had been sealed to a 14/20 ground glass joint, and Ph₃CH was added as an internal NMR integration standard. For runs 1–6, the tube was fitted with a vacuum stopcock, attached to a vacuum line, and evacuated, and C₆D₆ was then added by vacuum transfer. The tube was submitted to two freeze–pump–thaw cycles and then sealed with a torch. For runs 7–10 the C₆D₆ was added in the glovebox. The tubes were then attached to the vacuum line as above. The samples were heated (the NMR tubes were inverted) in a thermostated constant-temperature water bath. The volume (in mL) used to calculate the concentrations was determined according to the formula $V = \pi(0.213)^2h$, where h is the height in cm of the solution measured immediately after

removing the sample from the water bath. The NMR tube was cooled in water immediately after removing from the bath and centrifuged prior to recording each NMR spectrum. All data are collected in Table 1.

Kinetic runs of the decomposition of **1a** were analyzed by monitoring the disappearance of the combined MeCp singlets of the cis and trans isomers at δ 1.84 and 1.78, relative to the methine resonance of Ph₃CH at δ 5.41. Crossover experiments were analyzed by monitoring the appearance (or lack thereof) of the CH₃ doublet of **2b** at δ 0.27 ($J_{\text{PH}} = 6.7$ Hz). At 200 MHz, this doublet overlaps that due to **2a** (δ 0.30, $J_{\text{PH}} = 6.4$ Hz), giving the appearance of a triplet when the two are present in equal amounts. The extent of methyl exchange given in Table 1 is equal to the ratio of product to its equilibrium concentration and can be calculated according to eq 5, where

$$\begin{aligned} \% \text{ exchange} &= \mathbf{2b}/\mathbf{2b}_e = \mathbf{2b}/\mathbf{2b}_{t=\infty} = [\mathbf{2b}/(\mathbf{2a} + \mathbf{2b})]/ \\ & \quad \{[\text{MeCp}]/([\text{MeCp}] + [\text{Cp}])\}_{t=0} \\ &= [v_3/(v_1 + v_3)]/\{[\text{MeCp}]/([\text{MeCp}] + [\text{Cp}])\}_{t=0} \quad (5) \end{aligned}$$

$\{[\text{MeCp}]/([\text{MeCp}] + [\text{Cp}])\}_{t=0}$ is the initial percentage of MeCpFe starting materials, and will therefore also be equal to the MeCp products at equilibrium ($t = \infty$).⁴⁹ The relative amounts of **2a** and **2b** were estimated by comparison of the heights of the outer two peaks of the overlapping doublets, $v_1 = \sim 0.33$ ppm (**2a**), $v_2 = \sim 0.30$ ppm (**2a** + **2b**), and $v_3 = \sim 0.27$ ppm (**2b**). Integration, while somewhat qualitative due to the lack of baseline resolution of the three peaks, clearly showed that the height of v_2 was not an accurate indicator of its area.

The reaction of **1a** and **1b-d₃** in which the starting materials were isolated for mass spectral analysis (run 7) was carried out at the higher kinetic-run temperature (75 °C) than the other crossover reactions (65 °C) in order to facilitate calculation of the halfway point. Methyl exchange was verified, but then the unreacted starting materials were isolated by column chromatography on silica using benzene as the eluting solvent. A red band was collected and the solvent removed by vacuum. Mass spectra (electron impact, 140 °C source temperature) were obtained on the red solid at both 70 and 16 eV. At 70 eV, **1a** ($m/e = 382$) and **1b-d₃** ($m/e = 399$) were 8–9% of the base peak due to Cp(MeCp)Fe ($m/e = 200$), while crossover peaks due to **1a-d₃** ($m/e = 385$) and **1b** ($m/e = 396$) were not observed, each having an upper limit of 0.6% of the intensity of $m/e = 382, 399$; (MeCp)₂Fe ($m/e = 214$) was $\sim 77\%$ of the base peak, and Cp₂Fe was not observed. At 16 eV, the carbyne M⁺ peaks had the same absolute ion intensity as at 70 eV and were 50% of the new base peak due to CpFe(μ -CO)(μ -COCH₃)MnMeCp ($m/e = 326$); in addition MeCpFe(μ -CO)(μ -COCD₃)MnMeCp ($m/e = 343$) was 70% of the base peak. No crossover peaks due to **1b** (<0.7% of m/e 396 + 397) or MeCpFe(μ -CO)(μ -COCH₃)MnMeCp ($m/e = 340$) were observed, while a peak at $m/e = 385$, the same as crossover product **1a-d₃**, was 1.9% of $m/e = 382 + 383$ (the M⁺ and M⁺ + 1 peaks of **1a**), and a peak at $m/e = 329$, the same as crossover peak CpFe(μ -CO)(μ -COCD₃)MnMeCp, was 2.2% of $m/e = 326 + 327$ (the M⁺ and M⁺ + 1 peaks of the base peak).

Computer Modeling. The Fortran program CRK2005 is designed to allow a user to fit a set kinetic data to a set of differential equations; while the size of the problem can be increased without difficulty, the version in the Supporting Information is dimensioned for five kinetic runs, each having at most 30 time points, and a maximum of 30 variables (rate constants and variable initial reactant concentrations), 30 species with initial concentrations, and up to 11 species with observed concentrations specified at each time point. The program reads in data from user-generated files that contain information on the number of (1) differential equations, (2)

(49) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley-Interscience: New York, 1981.

observed species, (3) “steady-state” intermediates and their maximum concentration as a percent of reactant concentration, (4) rate constants, (5) reactant concentrations whose initial values will be allowed to be varied, and (6) kinetic runs, followed by for each run the number of time points, final time, and standard deviation for each concentration (see below). Initial guesses of rate constants are input, as are the identities of the reactant concentrations that will be varied and by how much; a separate data file of all initial reactant concentrations (including for instance all intermediates which are initially zero, and the initial value of [PPH₃]) followed by values of observed data points at each time is also input. The differential equations written in Fortran are included as a separate subroutine, and so the program must be compiled for each mechanism to be tested. The initial rate constants and reactant concentrations are then used to numerically integrate the rate equations out to the specified final time, using a published routine for fourth-order Runge–Kutta integration using adaptive step-size control in order to allow integration of rate constants that vary by more than 4 orders of magnitude (described as Runge–Kutta fifth-order quality-controlled steps).^{19,50} A subroutine then uses these integrated results to determine the calculated concentrations of each observed species at each time point. These calculated values are then compared to the observed values to give the error for the initial set of variables. The error function that was minimized is the reduced chi square function χ_v^2 (eq 6),⁵¹ where n is the number

$$\chi_v^2 = \left(\sum_{i=1}^n \frac{[c_i(\text{obs}) - c_i(\text{calcd})]^2}{\sigma_i^2} \right)^{1/2} \bigg/ \nu \quad (6)$$

$\nu = n - (\text{number of parameters})$

of nonzero data points, the number of parameters is the number of rate constants plus the number of initially varied reactant concentrations, $c_i(\text{obs})$ and $c_i(\text{calcd})$ are the observed

(50) Integration of such “stiff” differential equations in principle can be done using the Gear integration scheme, but our attempts using the IMSL, Inc. package were not successful. A package of PC programs written by T. Beukelman, R. J. McKinney, and F. J. Weigert (PRGEAR, GEAR, and GIT), available through Project SERAPHIM of the ACS, does implement the Gear scheme, and we have used this set of programs to check parts of our mechanisms.

(51) Bevington, P.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*, 3rd ed.; McGraw-Hill: New York, 2003.

and calculated concentrations, respectively, and σ_i is the estimated error in units of concentration for each run. This error estimate was computed on the basis of estimates in errors of weighing reactants, measurement of solvent volume, and NMR integration, and was assumed to be constant for each run. In practice, a “perfect” fit that involves only statistical error equal to this estimate of σ_i will give $\chi_v^2 \approx 1$. A value of χ_v^2 much less than 1 indicates that σ_i has been overestimated, while a value of χ_v^2 much greater than 1 indicates that σ_i has been underestimated or more likely that the mechanistic model is poor. To allow this statistical value to be compared to a more intuitive error estimate, a percent error was also calculated (eq 7) by dividing the standard deviation of the calculated

$$\% \text{ error} = \left(\sum_{i=1}^n \frac{([c_i(\text{obs}) - c_i(\text{calcd})]^2)^{1/2}}{\nu} \right) \bigg/ \sum_{i=1}^n c_i(\text{obs})/n \quad (7)$$

concentrations by the average concentration. Finally, the sensitivity of χ_v^2 to changes in each rate constant was determined by calculating the change in each rate constant required to give a 1% increase in χ_v^2 , and this is reported as the deviations in the rate constants in Figure 3 and Table S-4 in the Supporting Information. The output of CRK2005 includes a user-set number of calculated points per line for plotting, and 50 points per line was found to be adequate; the output was plotted using the program pro Fit 6.0.0.

Acknowledgment. Financial support for this work from Research Corporation, the UCLA Committee on Research, the Universitywide Energy Research Group, the donors of the Petroleum Research Fund, administered by the American Chemical Society, NSF Grant No. CHE-9096105, and the City University of New York PSC-CUNY Research Award program is gratefully acknowledged.

Supporting Information Available: Kinetic data for runs 1–6, 9, and 10, table of product yields, data for additional runs using **3a** and **3b**, kinetic details for the CpFe(CO)Me mechanism, differential equations for Scheme 6 and the CpFe(CO)Me mechanism, and a listing of the Fortran program CRK2005. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0502640